RI | 9330

REPORT OF INVESTIGATIONS/1990

Sealed Flask Test for Evaluating the Self-Heating Tendencies of Coals

By Yael Miron, Alex C. Smith, and Charles P. Lazzara

1910 ★ 80 YEARS ★ 1990

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

Mission: As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

Report of Investigations 9330

Sealed Flask Test for Evaluating the Self-Heating Tendencies of Coals

By Yael Miron, Alex C. Smith, and Charles P. Lazzara

UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary

BUREAU OF MINES
T S Ary, Director

Library of Congress Cataloging in Publication Data:

Miron, Yael.

Sealed flask test for evaluating the self-heating tendencies of coals / by Yael Miron, Alex C. Smith, and Charles P. Lazzara.

p. cm.—(Report of investigations; 9330)

Includes bibliographical references.

Supt. of Docs. no.: I 28.23:9330.

1. Coal—Combustion. 2. Combustion, Spontaneous. I. Smith, Alex C. II. Lazzara, Charles P. III. Title. IV. Series: Report of investigations (United States. Bureau of Mines); 9330.

TN23.U43 [TP325] [622 S—dc20] [622'.334} 90-2491 CIP

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	μm	micrometer
Btu/lb	British thermal unit per pound	mm Hg	millimeter of mercury
°C	degree Celsius	mV	millivolt
cm	centimeter	pct	percent
cm^3/min	cubic centimeter per minute	ppm	part per million
g	gram	psi	pound per square inch
h	hour	psia	pound per square inch, absolute
L	liter	V	volt
mL	milliliter		

SEALED FLASK TEST FOR EVALUATING THE SELF-HEATING TENDENCIES OF COALS

By Yael Miron,[1] Alex C. Smith,[2] and Charles P. Lazzara[3]

ABSTRACT

This report describes laboratory studies by the U.S. Bureau of Mines to determine the suitability of a static oxygen (O_2) adsorption test for evaluating the self-heating tendencies of coals. Reliable minimum self-heating temperature (SHT) values from adiabatic oven tests were used as standards for comparison and evaluation.

A suite of six coals was tested in the adiabatic oven and in sealed flasks. In the latter tests, both undried and dried samples, in a range of four particle sizes, were examined. Miniature pressure transducers monitored pressures in the flasks, and gas samples taken at the end of the tests quantified all the gases present.

An excellent correlation was found between the minimum SHT's and amounts of O_2 adsorbed over a 7-day period for dried coals, independent of particle size. In addition, a good correlation was obtained between the minimum SHT's and pressure changes in the flasks at the end of the test for the same coals, also independent of particle size. Based on these results, the sealed flask test can be reliably used to determine the self-heating tendency of a bituminous coal sample.

[1]Chemical engineer.
[2]Research chemist.
[3]Supervisory research chemist.
Pittsburgh Research Center, U.S. Bureau of Mines, Pittsburgh, PA.

INTRODUCTION

Spontaneous combustion in underground coal mines is highly hazardous because it can result in fires, loss of life, and loss of the mines involved. In large part, the danger associated with spontaneous combustion of coal inside mines is due to the nature of the self-heating process and to the location in which it starts, namely, inside gobs or piles of coal where it is hidden from sight. In many cases, heatings due to spontaneous combustion are not detected until they have reached a dangerous stage, whereby the coal has attained high temperature and is emitting smoke and even glowing.

Over the years, many studies have been conducted in order to identify the main causes of spontaneous combustion of coal and to find means for preventing its occurrence and alleviating its effects. It is now well known that the main cause of spontaneous combustion is the exothermic adsorption of O_2 and moisture by the coal. When the rate of heat released by the coal is higher than the rate of dissipation of this heat to the surroundings, the temperature of the coal rises and thermal runaway can eventually occur. Many factors, both intrinsic and extrinsic, including coal rank, particle size and size distribution, moisture content of coal, ventilation rate, partial pressure of O_2, percent humidity, geology of seam, and mining practices, combine to contribute to the spontaneous combustion process. Since the initial stages of self-heating are not easily detected, it is essential to identify the coals that are highly susceptible to self-heating so as to be able to take precautionary steps to prevent the occurrence of fires.

Various test methods are used to assess the relative tendencies of coals to self-heat. These methods include crossing point temperature (CPT) (*1*),[4] differential thermal analysis (*2*), adiabatic calorimetry (*3-9*), and O_2 adsorption, among others (*10-19*). These tests all have advantages and drawbacks, as far as duplicating actual mine conditions during the development of spontaneous combustion events. Some of the tests have been examined and evaluated in detail as to their accuracy and validity (*20-25*). Although it is recognized that coal oxidation is only one factor in the development of spontaneous combustion and that mining factors are significant in determining whether spontaneous combustion will occur in a mine (*26-28*), it is still useful to assess the relative susceptibility of a coal to self-heat, especially as a guide to selecting mining methods and procedures.

Two test methods have been used extensively by the U.S. Bureau of Mines, as well as by others, to examine the self-heating of coal—adiabatic calorimetry and static O_2 adsorption (*3-4*). Minimum SHT's, ranging from 35° to 135° C, were determined in the Bureau's adiabatic oven for various coals. The minimum SHT is the minimum initial temperature that produces a sustained exothermic reaction at the conditions of the test in the adiabatic oven. The SHT's were then used to rank the relative self-heating potentials of the coals, and an empirical expression was derived that predicts a bituminous coal's minimum SHT in the adiabatic oven based on the coal's dry ash-free O_2 content (*4*).

The other test used widely over the years at the Bureau to measure the reactivity of coal is static O_2 adsorption (*3*). In this test, a coal sample is placed in a sealed flask and gas samples are withdrawn daily for analysis. The results are then used for the determination of the rates of O_2 adsorption. This method has the drawback that when the volume of the flask is small, frequent removal of samples depletes available O_2 and also complicates calculations. An alternative method is to measure the amount of O_2 adsorbed by a specified mass of coal in a specified time at which a quasi-equilibrium has been established. Since the rates and amounts of O_2 adsorbed have been found to be a function of coal composition and its content of organic oxygen moieties, this test could be used as a relative measure of the reactivity of the coal. Although heat release rates by the coal samples are not measured in this test, the implicit assumption is that the rate of heat generation is proportional to the amount of O_2 adsorbed by the coal. The organic oxygen groups that are the main sites for O_2 adsorption (*29*) have also been correlated with the minimum SHT's of bituminous coals determined in the adiabatic oven. Thus, both tests, adiabatic calorimetry and static O_2 adsorption, essentially measure the same parameter—the active oxygen-containing sites on the coal.

To determine the minimum SHT of a coal, at least two tests in the adiabatic oven are required, and at times, three or four tests have to be conducted. These tests are quite lengthy, and in addition, the coal has to be shipped from the mine to the laboratory. It would be useful to have a simple and reliable test to assess the tendency of a coal to self-heat, which could be conducted at the mine and could be used to predict the minimum SHT of the coal.

[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

As part of its program to improve safety in mining, the Bureau conducted this research to find if any or some of the parameters determined in the sealed flask tests correlate with the minimum SHT values determined in the adiabatic oven for the same coals. These SHT values have been shown to be reliable and reproducible predictors of the self-heating tendency of a coal. Finding a good correlation, the sealed flask test could then be modified for use in the field.

A suite of six bituminous coals with minimum SHT values ranging from 35° to 105° C was selected for the tests in the adiabatic oven and in sealed flasks adapted for these tests.

TEST MATERIALS

Fresh coal samples from the various mines were selected by the mine personnel. The samples consisted mostly of large lumps, 10 to 20 cm in size. These samples were shipped inside plastic bags that were tightly sealed to exclude air. The coals were selected on the basis of results of previous adiabatic oven tests with coals from the same mines to cover a wide range of self-heating potentials and ranks of coal. The minimum SHT's of these coals, determined in earlier tests, varied from 35° to 135° C (*4*). The coals and their analyses are listed in table 1.

ADIABATIC OVEN STUDIES

EXPERIMENTAL PROCEDURES

The relative self-heating tendencies of the six coal samples were evaluated in the adiabatic oven. Figure 1 is a schematic of the oven and sample container. The oven is designed to minimize heat losses from the coal sample during the self-heating stage of the test.

The sample is contained in a cylindrical brass wire mesh basket, 7.6 cm in diameter by 5 cm high, which is enclosed in a stainless steel assembly. Preheated, humidified air enters the bottom of the assembly, passes through the sample, and exits at the top. A stainless steel cylinder surrounded by a nickel-chromium wire resistance heater serves as the sample oven. The cylinder surrounds the sample assembly and is attached to an insulated top cover in which another resistance-type heater, wired in parallel to the sample oven, is located.

The oven assembly is contained in a 15-cm-ID Dewar flask that is surrounded by a 5-cm layer of insulation in which another heater is embedded. The apparatus is instrumented to record sample and oven temperatures and O_2 and carbon monoxide (CO) concentrations in the exit gas stream. A more detailed description of the apparatus is found in an earlier report (*4*).

Table 1.—Analyses of coal samples as received, by order of minimum SHT

	No. 80, WY	F, CO	No. 6, IL	Pittsburgh, PA	Mary Lee, AL	Pocahontas 3, VA
Proximate analysis, wt pct:						
Moisture	10.3	10.4	7.9	1.8	1.2	0.9
Volatile matter	39.1	38.9	34.6	38.1	26.5	17.6
Fixed carbon	46.2	42.1	36.1	55.7	60.4	78.3
Ash	4.4	8.7	21.4	4.4	12.0	3.2
Ultimate analysis, wt pct:						
Hydrogen	5.7	5.8	4.9	5.5	4.7	4.5
Carbon	64.7	61.8	53.7	79.4	76.1	87.4
Nitrogen	1.6	1.3	1.1	1.6	1.8	1.2
Sulfur	0.4	0.3	5.2	1.1	1.1	0.6
Oxygen	23.2	22.2	13.6	8.0	4.4	3.1
Oxygen, DAF	16.5	16.0	9.3	6.8	3.8	2.4
Heating value, Btu/lb	11,270	10,861	9,804	14,109	13,469	14,988

DAF Dry ash-free.

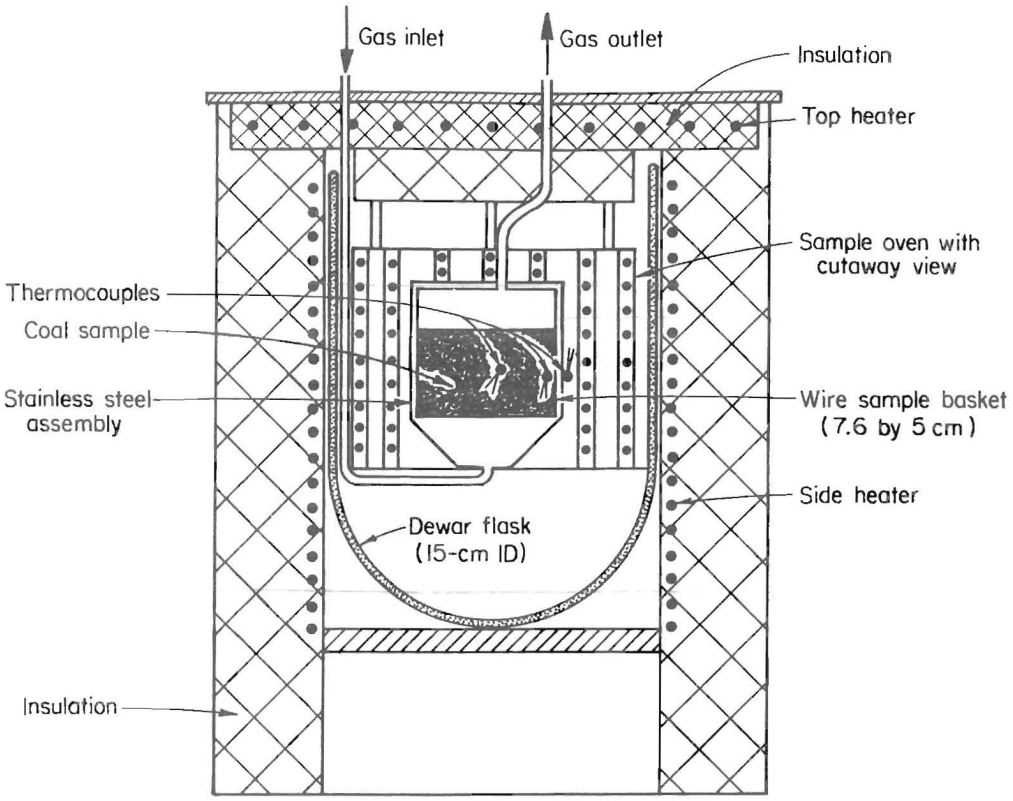

Figure 1.—Schematic of adiabatic oven.

The evaluation of the self-heating tendency of a coal by the determination of the coal's minimum SHT was made using a set of standard experimental conditions and methods described in reference 4. These conditions were determined to be the most stringent conditions for self-heating to occur in the adiabatic oven. The lump coal, received fresh from the mine, was pulverized and the minus 100- plus 200-mesh (150 by 75 μm) fraction was dried in an oven at 67° C under a flow of dry nitrogen (N_2). A 100-g sample was placed in the adiabatic oven and brought to a preselected initial temperature under a 200-cm^3/min flow of dry N_2. The coal was then exposed to a 200-cm^3/min flow of humidified air. A series of tests was made, each test with a fresh sample, in 5° C increments, until the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway, was determined.

EXPERIMENTAL RESULTS

The minimum SHT's and relative self-heating tendencies of the six coals are listed in table 2. The temperatures ranged from 35° C for the No. 80 and F coals to 105° C for the Mary Lee and Pocahontas 3 coals. The relative self-heating tendencies were assigned based on the criteria determined in reference 4: (1) a high self-heating tendency for coals with minimum SHT's <70° C, (2) a medium self-heating tendency for coals with minimum SHT's between 70° and 100° C, and (3) a low self-heating tendency for coals that have minimum SHT's >100° C. The minimum SHT's are a relative measure of the self-heating tendency of the coal only and do not take into account other important contributing factors associated with the spontaneous combustion process in actual mining conditions.

Figure 2 shows the temperature-time traces of the tests to determine the minimum SHT of the F coal. At a starting temperature of 30° C, there was a rise in the coal sample temperature to 76° C in about 10 h after exposure to moist air. The temperature then leveled off and eventually the sample cooled. In another test, with a fresh sample at an initial temperature of 35° C, the sample temperature

increased steadily, reaching thermal runaway (150° C) in just over 20 h. The test was terminated at 150° C to protect the apparatus. The effect of increasing the initial temperature is seen in the third curve. From an initial temperature of 40° C, the sample self-heated in just 8 h, showing the dependence of the coal oxidation rate on temperature. Thus, the minimum SHT of the F coal was 35° C.

Table 2.—Minimum SHT's of coal samples evaluated in adiabatic oven and their relative self-heating tendencies

Coal sample	Apparent rank[1]	Minimum SHT, °C	Relative self-heating tendency
No. 80	hvCb	35	High.
F	hvCb	35	Do.
No. 6	hvCb	65	Do.
Pittsburgh	hvAb	85	Medium.
Mary Lee	mvb	105	Low.
Pocahontas 3	lvb	105	Low.

[1]Rank based on ASTM D388-82 classification system (*30*): hvCb, high-volatile C bituminous; hvAb, high-volatile A bituminous; mvb, medium-volatile bituminous; lvb, low-volatile bituminous.

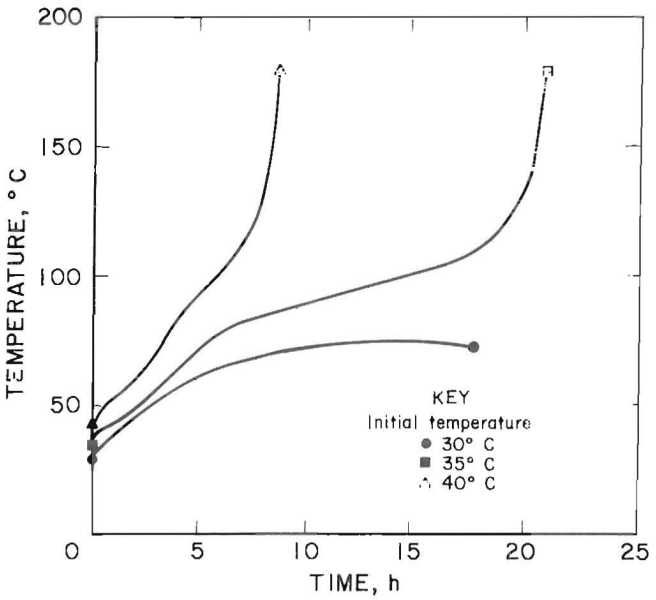

Figure 2.—Temperature histories in self-heating tests with F coal at initial temperatures of 30°, 35°, and 40° C.

SEALED FLASK STUDIES

EXPERIMENTAL PROCEDURES

The coal samples were contained in six 500-mL Erlenmeyer flasks that were modified to accommodate a pressure transducer and a gas sampling port. A ground glass socket joint (ℸ28/12) was attached to the flask neck, and a matching ball joint was adapted to hold a miniature pressure transducer. A short side arm fitted with a puncture-type silicon septum was provided for repetitive retrieval of gas samples with a fine syringe needle. A test flask is shown in figure 3.

An absolute-type, miniature, solid-state piezoresistive pressure transducer (Omega PX 136)[5] was used to measure the pressure in the flask. The output was in millivolt units, with 100 mV equal to 775.5 mm Hg (15 psia). The pressure range of the transducer is 0 to 15 psia, but it can sustain an overpressure of 45 psi. Push-on connectors with crimp contacts attach to the four terminals (interface pins) on the transducers to supply them with 10-V dc power and at the same time to transmit the millivolt output to a digital transducer indicator. Power was continuously supplied to the six transducers while output was read, as desired, from each pressure transducer, one at a time with a 10-position rotary switch. The complete assembly of the six flasks with instrumentation is shown in figure 4.

Samples for the tests were freshly ground, as needed, in a general-purpose grinding mill and then sieved to the desired size fractions. In tests with undried samples, the coal was ground and sieved, and 50-g samples were sealed in the flasks with as little delay as possible. Pressure readings were taken before and immediately after the flasks were sealed, and thereafter, at various intervals, depending on the rate of pressure change. Tests were conducted in triplicate, and two size fractions were tested at the same time, for a total of six samples. Pressures inside the flasks and ambient temperature were monitored for 7 days. At the end of the test period, gas samples were taken from each flask for analysis by gas chromatography. The flasks were then emptied and cleaned in preparation for fresh samples.

In tests with dried samples, the ground and sieved fractions were promptly placed in drying towers and dried to a constant weight at 67° C under a flow of dry N_2 before they were weighed and placed in the flasks. The dried samples were then tested in the same manner as were the undried samples.

[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

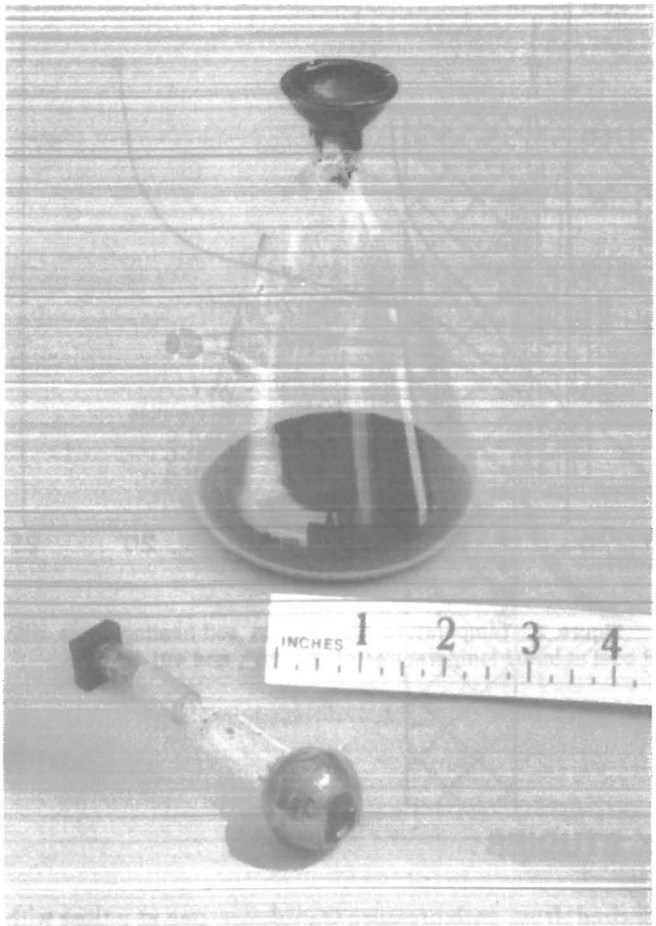

Figure 3.—Sealed flask test apparatus.

The four particle size fractions tested were the following: (1) 1,200 by 600 μm (minus 16- plus 30-mesh), (2) 600 by 300 μm (minus 30- plus 50-mesh), (3) 300 by 150 μm (minus 50- plus 100-mesh), and (4) 150 by 75 μm (minus 100- plus 200-mesh).

EXPERIMENTAL RESULTS

Gaseous Compositions

The parameters determined in the sealed flask experiments were the compositions of the gaseous atmospheres inside the flasks after 7 days of exposure and the cumulative and total pressure drops inside the flasks for the tests' duration of 7 days.

The gaseous compositions found in the flasks after 7 days for the undried samples are shown in table 3 for the six coals, as a function of the size fractions. Only gases of interest are shown, namely O_2, carbon dioxide (CO_2), CO, methane (CH_4), and ethane (C_2H_6). In addition, the amounts of O_2 adsorbed and CO index values are also presented, where the CO index is the ratio of CO released in parts per million to O_2 adsorbed in volume percent. The values are the averages calculated for the sets of triplicate samples, which were very reproducible.

Likewise, the gaseous compositions found in the flasks containing the dried coal samples, as well as the amounts of O_2 adsorbed and CO index values, are shown in table 4. Again, the values shown are the average values for triplicate samples; these values were very reproducible.

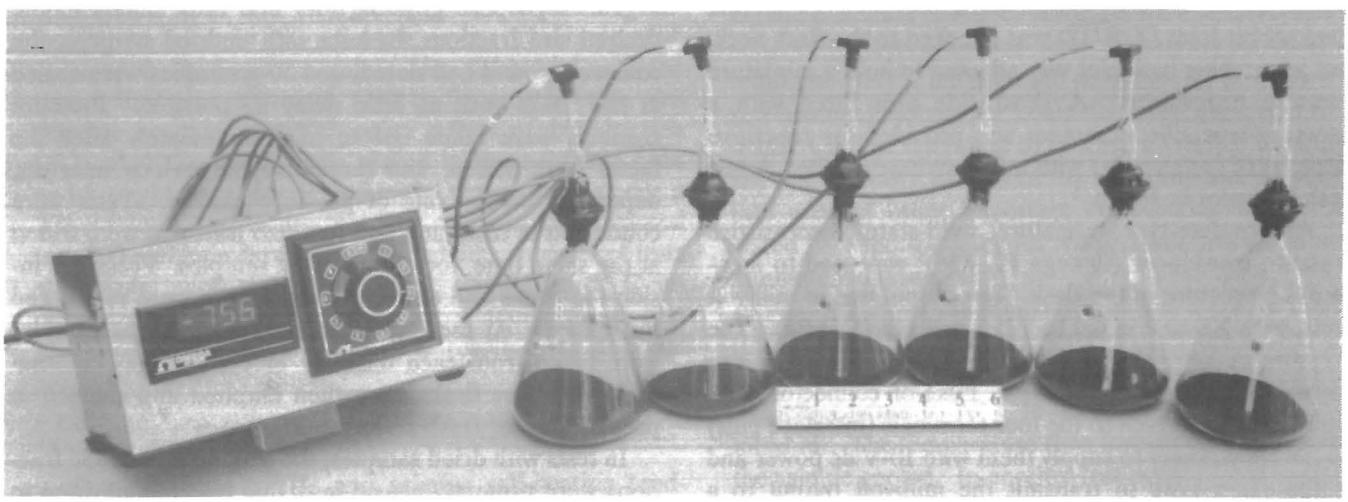

Figure 4.—Complete sealed flask assembly of six flasks with instrumentation.

Table 3.—Average gas compositions in sealed flasks containing undried coal samples after 7 days

Coal sample	Fraction tested, μm	Gas composition					O_2 adsorbed, vol pct	CO index[1]
		O_2, vol pct	CO_2, vol pct	CO, ppm	CH_4, vol pct	C_2H_6, ppm		
No. 80	1,200 by 600	3.2	0.75	1,880	0.003	4	17.7	106
	600 by 300	.7	.75	2,123	.002	3	20.2	105
	300 by 150	.7	.79	2,420	.001	3	20.3	119
	150 by 75	.6	.86	2,523	.001	3	20.4	124
F	1,200 by 600	2.3	.78	2,863	2.58	304	18.7	153
	600 by 300	.3	.93	3,197	1.70	406	20.6	155
	300 by 150	.3	.91	3,450	.68	316	20.6	167
	150 by 75	1.3	.87	3,990	.24	177	19.7	203
No. 6	1,200 by 600	2.0	.84	751	7.33	817	19.0	40
	600 by 300	.3	.63	830	4.97	948	20.7	40
	300 by 150	.3	.52	718	1.84	993	20.7	35
	150 by 75	.3	.53	684	.43	774	20.7	33
Pittsburgh	1,200 by 600	15.1	.52	331	.003	2	5.9	56
	600 by 300	14.7	.45	389	.003	2	6.3	62
	300 by 150	14.3	.42	495	.003	3	6.7	74
	150 by 75	14.0	.27	560	.002	3	6.9	81
Mary Lee	1,200 by 600	12.3	.23	240	16.21	83	8.7	28
	600 by 300	13.2	.21	268	13.22	92	7.8	34
	300 by 150	18.8	.09	154	3.31	71	2.2	70
	150 by 75	19.1	.09	158	1.66	63	1.9	83
Pocahontas 3	1,200 by 600	19.5	.10	73	3.21	10,367	1.5	49
	600 by 300	19.5	.09	67	2.97	12,033	1.4	48
	300 by 150	19.8	.09	85	1.89	13,477	1.2	71
	150 by 75	19.9	.09	83	.83	11,367	1.0	83

[1] CO index = $\frac{\text{CO, ppm}}{O_2 \text{ adsorbed, vol pct}}$.

The results for the undried coal samples were partly unexpected (table 3). Four of the coals—F, No. 6, Mary Lee, and Pocahontas 3—released significant amounts of CH_4, and Pocahontas 3 coal also released significant amounts of C_2H_6. The amounts of hydrocarbons released by Mary Lee and Pocahontas 3 coals exceeded the amounts of O_2 adsorbed. The amount of CH_4 released by the four coals decreased with decreasing particle size. Apparently, grinding the coal to the finer sizes released most of the CH_4 during the sample preparation phase.

The amount of O_2 adsorbed by either the dried or undried coal samples was most significant in this study because adsorption of O_2 by the coal is the main cause of self-heating. The amount of O_2 adsorbed by the undried samples of No. 80, F, and No. 6 coals, as seen in table 3, followed a similar pattern. The coarsest fraction adsorbed somewhat less O_2 than was adsorbed by the three finer fractions; the latter three fractions essentially adsorbed all the O_2 initially present in the flasks with the exception of the finest fraction of the F coal, which adsorbed somewhat less than the two intermediate fractions. The amount of O_2 adsorbed by the Pittsburgh coal increased monotonically, but not significantly, with decreasing particle size, from 5.9 to 6.9 vol pct from the coarsest to the finest fraction. Finally, the amounts of O_2 adsorbed by the Mary Lee and Pocahontas 3 coals decreased with decreasing particle size, a trend opposite to the trend shown for the other four coals. The decrease was minimal for the Pocahontas 3 coal, which adsorbed from 1.5 to 1.0 vol pct O_2, over the size fractions tested. The decrease in the amount of O_2 adsorbed by Mary Lee coal with decreasing particle size was much more pronounced; it fell from 8.7 to 1.9 vol pct O_2. In summary, it was seen that the different coals interacted quite differently and uniquely with O_2.

Table 4.—Average gas compositions in sealed flasks containing dried coal samples after 7 days

Coal sample	Fraction tested, μm	Gas composition					O_2 adsorbed, vol pct	CO index[1]
		O_2, vol pct	CO_2, vol pct	CO, ppm	CH_4, ppm	C_2H_6, ppm		
No. 80	1,200 by 600	0.2	0.06	2,800	12	0	20.8	135
	600 by 300	.4	.05	2,703	11	0	20.6	131
	300 by 150	.3	.09	3,153	15	0	20.6	153
	150 by 75	.6	.11	3,237	11	0	20.4	159
F	1,200 by 600	1.2	.05	3,483	17	3	19.7	177
	600 by 300	1.7	.05	3,727	14	1	19.2	194
	300 by 150	1.7	.11	4,543	15	0	19.3	235
	150 by 75	.9	.14	4,660	12	0	20.1	232
No. 6	1,200 by 600	6.9	.06	1,460	22	3	14.1	104
	600 by 300	7.3	.07	1,350	23	2	13.7	99
	300 by 150	3.9	.13	1,777	26	2	17.1	104
	150 by 75	5.0	.13	1,780	26	2	16.0	111
Pittsburgh	1,200 by 600	13.1	.07	785	10	1	7.8	101
	600 by 300	13.6	.06	822	10	0	7.3	113
	300 by 150	13.9	.07	752	20	1	7.1	106
	150 by 75	13.2	.08	913	14	1	7.8	117
Mary Lee	1,200 by 600	17.0	.04	419	556	8	4.0	105
	600 by 300	17.1	.04	475	28	6	3.9	122
	300 by 150	18.1	.04	396	10	3	2.9	137
	150 by 75	18.3	.04	397	10	0	2.7	147
Pocahontas 3	1,200 by 600	18.2	.05	239	3,360	2,184	2.8	85
	600 by 300	18.3	.05	243	560	2,160	2.6	93
	300 by 150	18.4	.06	331	14	536	2.6	127
	150 by 75	18.6	.06	332	19	42	2.4	138

[1] CO index = $\frac{\text{CO, ppm}}{O_2 \text{ adsorbed, vol pct}}$.

The next two gases of interest were CO_2 and CO. These gases, together with water (H_2O), are generally accepted as the major gaseous oxidation products of coal. Although both CO and CO_2 have been recommended for use as indicators of incipient combustion in coal mines, CO is the gas usually monitored in the mines, and the CO index is used at times as an indicator for heating events. The amount of CO_2 released by the undried coals was in all the cases larger than the amount of CO released by them. And in all cases, the less O_2 adsorbed, the less CO and CO_2 released. Also, the combined amounts of CO and CO_2 emitted by the samples were much smaller than the amount of O_2 adsorbed, in agreement with the results of other investigators.

The effect of particle size on the amount of CO released by the undried fractions was mixed. The amount of CO released increased with decreasing particle size for the No. 80, F, and Pittsburgh coals. The amount of CO released by Pocahontas 3 coal was very small, and within experimental error, did not change with changing particle size. Results of CO released by the No. 6 and Mary Lee coals were mixed with respect to particle size, but in general, the amount decreased with decreasing particle size, with the exception of amounts of CO for the 600- by 300-μm size fraction. Amounts of CO_2 released by Pittsburgh, No. 6, and Mary Lee coals decreased with decreasing particle size. The amount of CO_2 released by the Pocahontas 3 coal was essentially the same for all the size fractions tested, while it increased slightly with decreasing particle size for No. 80 coal. Results were mixed for the F coal.

In summary, a general trend was not found for either O_2 adsorption or for the release of CO or CO_2 by these six coals. Each coal behaved in a distinctive manner.

Ratios of CO_2 to CO were calculated for all the test samples. These ratios declined in value with decreasing particle size for all the undried samples, whereas the reverse trend was found for four of the dried coal samples. The ratios for the dried Pittsburgh coal did not vary with particle size, and these ratios decreased with decreasing size for the dried Pocahontas 3 samples. During the preparation of the coal samples, it was noted that the amount of water in the samples decreased somewhat with grinding, as is expected. However, the amount of moisture remaining in the undried coal samples was sufficient to retain the relatively large amounts of CO_2.

The ratio of CO emitted to O_2 adsorbed, (CO-ΔO_2), known as the CO index, has been proposed as a means for assessing the spontaneous combustion susceptibility of coals. In sealed flask tests with dried coals, CO index values >180 were characteristic of coals most susceptible to self-heating (*3*). CO index values were calculated for the atmospheres in the sealed flasks with undried samples at the end of 7 days. Values lower than 100 were obtained for four coals—No. 6, Pittsburgh, Mary Lee, and Pocahontas 3—for all size fractions. Values for No. 80 coal were somewhat higher than 100. The highest values, ranging from 150 to 200, were obtained for the F coal, suggesting that of the six coals it was the most susceptible to self-heating. These values increased with decreasing particle size for all but the No. 6 coal. Since test conditions, including flask volume and particle size range varied for these two studies, only qualitative comparisons are valid.

Results for O_2 adsorption and gas release values for the dried samples were different in many respects from results obtained for the undried coals. Drying and/or the flow of N_2 through the samples during the drying phase essentially eliminated the CH_4 and C_2H_6 from three of the coals (F, No. 6, and Mary Lee) that emitted large amounts of these hydrocarbons in the undried state. The amounts of CH_4 and C_2H_6 released by the Pocahontas 3 coal were also reduced to a great extent, especially for the finer fractions. Likewise, the amounts of CO_2 released by all six coals were sharply reduced, in most cases by about an order of magnitude.

The dried No. 80 and F coals, like the undried samples, adsorbed almost all or all of the available O_2 so that the effect of particle size could not be discerned. The amounts of O_2 adsorbed by Pittsburgh and Pocahontas 3 coals were slightly larger than the amounts adsorbed by their undried counterparts, and the effects of particle size were small. Slightly less O_2 was adsorbed by the smaller particle sizes of both the dried and undried Pocahontas 3 samples. Unexpectedly, the dried No. 6 and Mary Lee coals adsorbed less O_2 than the undried samples, especially the coarse size fractions. Also, for the Mary Lee coal, an inverse relation was found between O_2 adsorption and particle size for both dried and undried samples.

In summary, removal of moisture, CO_2, and hydrocarbons, when present, by drying and/or by flushing N_2 through the coal during the drying time, slightly increased O_2 uptake by the Pittsburgh and Pocahontas 3 coals, while decreasing O_2 uptake noticeably for the No. 6 coal and the coarse size fractions of Mary Lee coal, and to a lesser extent for the finer size fractions of Mary Lee coal.

The amounts of CO given off by the dried samples generally increased for all six coals, as compared with the amounts given off by the undried samples, and in most cases they doubled. Also, except for the Pittsburgh and Mary Lee coals, the finer size fractions of the other four coals emitted more CO than the coarse size fractions. The combined amounts of CO and CO_2 released by all the dried samples were very much smaller than the amounts of O_2 adsorbed. Finally, most CO index values were above 100, and in general, they increased with decreasing particle sizes, as did the CO index values for the undried samples. The highest CO index values were again found for the F coal.

Pressure Changes in Flasks

In general, the quantities of the gases released by the coals due to O_2 adsorption, namely CO_2, CO, and H_2O, were much smaller than the amounts of O_2 adsorbed. Thus, it was thought that pressure measurements could be utilized for observing the quantity and rate of O_2 adsorbed. As it turned out, four of the undried coals emitted large amounts of hydrocarbons, and pressure changes inside the flasks containing these coals did not correspond directly with the changes in O_2 concentration.

When the coal samples were dried, most of the hydrocarbons were removed from the coals. In addition, the quantities of CO_2 released were much smaller. Therefore, pressure changes in the flasks reflected the amounts of O_2 adsorbed. Average values of the pressure changes for the dried samples for periods of 24, 48, 72, and 168 h (ΔP_1, ΔP_2, ΔP_3, and ΔP_7, respectively) from the start of each test are presented in table 5 and are shown in figures 5 and 6 for the 150 by 75 μm and 1,200 by 600 μm size fractions, respectively. The ΔP_1, ΔP_2, and ΔP_3 values were evaluated to determine if the propensity of a coal to self-heat owing to O_2 adsorption could be identified within a relatively short time of 1, 2, or 3 days, or if 7 days would be required.

Pocahontas 3 coal released up to 0.3 vol pct CH_4 and 0.2 vol pct C_2H_6, even after it was dried. As a result, the presence of these gases influenced the pressure reading slightly. The pressure drops indicated for the No. 80 and F coals, which adsorbed all the available O_2, were somewhat higher than the theoretical amounts, based on total adsorption of O_2. Moisture adsorption from the air by these two reactive coals may have contributed to the higher pressure change values. Ambient temperatures during these tests varied at times between 20° and 25° C. Vapor pressures of water in air at these temperatures vary between 17.5 and 25.2 mm Hg, and these amounts are of the same order as denoted by the excess pressure readings, above the theoretical values for O_2. The amount of moisture adsorbed by the less reactive coals was much smaller. Temperatures and humidity conditions could have been more strictly controlled, but the purpose of this study was to determine if a relatively simple and inexpensive O_2 adsorption test would correlate with results of minimum SHT values for the corresponding coals. Such a test could be readily conducted at the mine site.

Table 5.—Average pressure changes in sealed flasks containing dried coal samples after 1, 2, 3, and 7 days

Coal sample	Fraction tested, μm	Pressure change, mm Hg			
		ΔP_1	ΔP_2	ΔP_3	ΔP_7
No. 80	1,200 by 600	133.4	162.1	175.3	186.9
	600 by 300	164.4	186.1	191.5	193.9
	300 by 150	135.7	159.0	169.8	171.4
	150 by 75	120.2	145.0	162.1	166.0
F	1,200 by 600	163.6	171.4	171.4	178.4
	600 by 300	176.8	179.9	179.9	186.9
	300 by 150	146.6	161.3	169.1	162.1
	150 by 75	145.0	171.4	169.1	163.6
No. 6	1,200 by 600	50.4	68.2	76.8	109.3
	600 by 300	58.9	76.8	85.3	117.9
	300 by 150	73.7	97.7	105.5	143.5
	150 by 75	69.0	91.5	100.0	138.0
Pittsburgh	1,200 by 600	45.0	61.3	68.2	92.3
	600 by 300	43.4	58.2	62.8	84.5
	300 by 150	21.7	30.2	37.2	58.9
	150 by 75	27.9	37.2	45.0	67.5
Mary Lee	1,200 by 600	45.0	53.5	58.9	69.0
	600 by 300	44.2	51.2	56.6	67.5
	300 by 150	32.6	34.1	37.2	47.3
	150 by 75	28.7	30.2	33.3	44.2
Pocahontas 3	1,200 by 600	34.1	31.0	46.5	38.0
	600 by 300	45.0	40.3	55.8	45.6
	300 by 150	41.1	45.8	47.3	49.6
	150 by 75	43.4	48.1	48.9	52.0

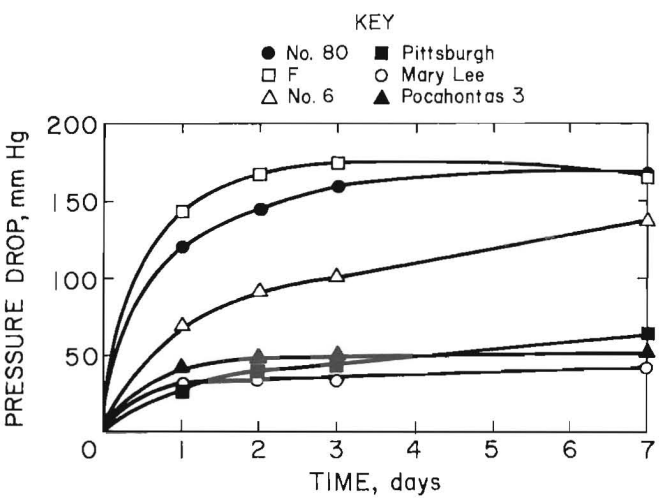

Figure 5.—Pressure drops in sealed flasks as function of time for 150 by 75 μm fractions of dried coals.

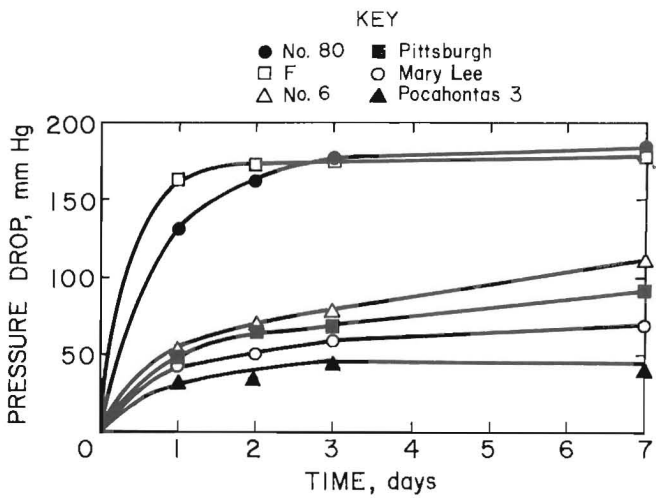

Figure 6.—Pressure drops in sealed flasks as function of time for 1,200 by 600 μm fractions of dried coals.

STATISTICAL CORRELATIONS OF TEST RESULTS

A multivariable linear regression analysis was conducted to determine if any correlation exists between the minimum SHT values found in the adiabatic oven tests and the various gases found in the atmospheres of the sealed flasks at the end of 7 days. Correlations were sought for both the dried and undried samples for each size fraction and for all sizes combined. If any correlation exists, then the sealed flask test procedure could be used to predict a coal's susceptibility to spontaneous combustion.

The computational method used in the regression analysis was a forward stepwise regression model based on the method given by Draper (*31*). The computer software used in the analysis is described by BBN Research Systems (*32*). The procedure involved inserting variables into the model in an order determined by using the partial correlation coefficient as a measure of significance. After the introduction of a variable in the model, an examination of the contribution made by each variable in the model was made using the F-test, and any variable making a nonsignificant contribution was removed. The process continued until no variables were added to or removed from the model.

The variables used in the calculations were the amounts of O_2 adsorbed, the concentration of CO, CO_2, and CH_4 in the flasks at the end of the test periods, and the CO index values calculated for the same times.

For the dried coal samples, the best correlation was found to be between the minimum SHT values determined in the adiabatic oven and the amounts of O_2 adsorbed in the sealed flasks. Additionally, this correlation between minimum SHT values and amounts of O_2 adsorbed was determined to be independent of particle size below 1,200 μm:

Size fraction, μm	*Correlation coefficient*
1,200 by 600	0.996
600 by 300	.973
300 by 150	.995
150 by 75	.987
All	.986

The resulting model for particle sizes <1,200 μm was

$$SHT_{min} = 116.6 - (3.9 \times \text{vol pct } O_2 \text{ adsorbed}). \quad (1)$$

This expression had a correlation coefficient of 0.986 with a standard deviation of regression of 1.04 and an average relative error of 6.0 pct. The minimum SHT's predicted from this model for the six coals are shown in table 6.

Table 6.—Experimental and predicted minimum SHT's, degree Celsius, for dried coal samples based on amounts of O_2 adsorbed in 7 days

	No. 80	F	No. 6	Pitts-burgh	Mary Lee	Poca-hontas 3
Experimental	35	35	65	85	105	105
Predicted,[1] fraction tested, μm:						
1,200 by 600 . .	35	39	61	86	101	106
600 by 300	36	41	63	88	101	106
300 by 150	36	41	50	89	105	106
150 by 75	37	38	54	86	106	107

[1]Based on SHT_{min} = 116.6 - (3.9 × vol pct O_2 adsorbed).

As can be seen, the predicted results for all six coals agree quite well with the experimental values for all size fractions. A plot of the predicted versus the experimental SHT's for these coals, based on equation 1, is shown in figure 7. Based on these results, an O_2 adsorption test in a sealed container can be developed that can utilize any particle size below 1,200 μm.

A separate regression analysis was also conducted using the CO index as the dependent variable and the minimum

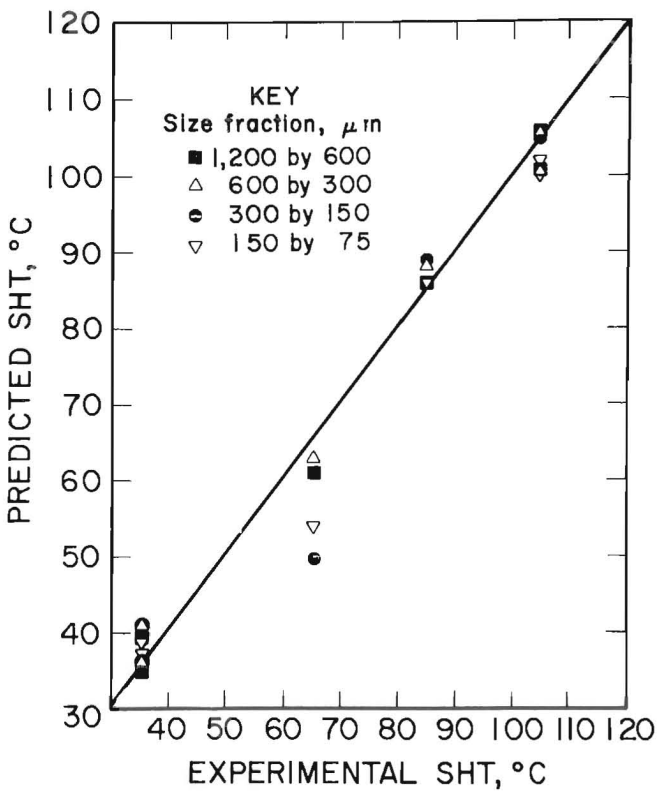

Figure 7.—Predicted versus experimental minimum SHT's of six coals based on amounts of O_2 adsorbed in 7 days.

SHT as the independent variable. The results are shown below:

Size fraction, μm	*Correlation coefficient*	
	Dried	*Undried*
1,200 by 600	0.83	0.84
600 by 300	.58	.83
300 by 150	.66	.66
150 by 75	.57	.60

A poor correlation was found, and the correlation worsened with decreasing particle size. Thus, it appears that the CO index is not a reliable indicator of the susceptibility of a coal to self-heat.

Another important correlation was that between pressure change in the flasks and O_2 adsorbed by the coal. If the pressure change corresponded to the amount of O_2 adsorbed by the coal, then it could be used to predict the minimum SHT of a coal. Correlation coefficients for the dried coals, for the four size fractions, as well as for all size fractions combined were obtained for pressure changes at the end of 7 days, ΔP_7:

Size fraction, μm	*Correlation coefficient*
1,200 by 600	0.976
600 by 300	.987
300 by 150	.991
150 by 75	.993
All	.980

Correlations improved with decreasing particle size, and the correlation coefficient for the combined samples was excellent (0.98).

Finally, the most desired correlation was one between the minimum SHT and pressure change values. Pressure change data were available over the entire test period, so separate regression analyses were conducted using ΔP_1, ΔP_2, ΔP_3, and ΔP_7 as the dependent variables and minimum SHT as the independent variable. The best fit was obtained for the ΔP_7 values, independent of particle size:

$$SHT_{min} = 128.9 - (0.52 \times \text{mm Hg } \Delta P_7). \quad (2)$$

The correlation coefficient for this model was 0.972, with an average relative error of 9.8 pct. The predicted minimum SHT's, based on equation 2, versus the experimental minimum SHT's, obtained in the adiabatic oven, are shown in figure 8. The scatter in the predicted SHT data is due mostly to the presence of moisture in the air during the tests, as discussed earlier. In addition, the pressure transducers are sensitive to changes in ambient temperature, which can introduce error. The correlation

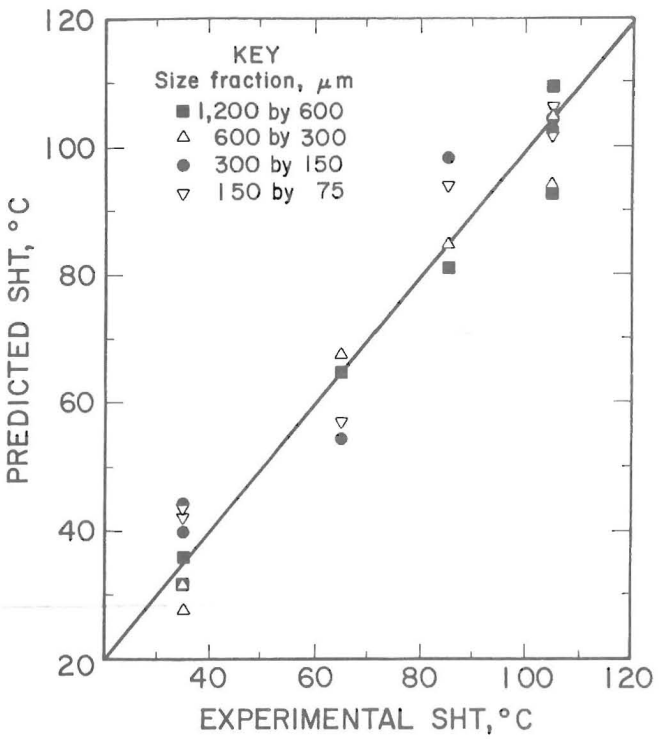

Figure 8.—Predicted versus experimental minimum SHT's of six coals based on pressure change, ΔP_7.

coefficients for ΔP_1, ΔP_2, and ΔP_3, for all sizes, were 0.910, 0.948, and 0.951, respectively. Hence, the correlation improved with test duration, and it is possible that a period <7 days would be adequate to reliably predict the minimum SHT of a coal.

Consequently, equation 2 can be used to predict the relative self-heating potential of coals. If ΔP_7 is >114 mm Hg, corresponding to a minimum SHT <70° C in the adiabatic oven, the coal would be assigned a high self-heating potential; if ΔP_7 is between 56 and 114 mm Hg, corresponding to a minimum SHT between 70° and 100° C, the coal would be assigned a medium self-heating potential; and if ΔP_7 is <56 mm Hg, corresponding to a minimum SHT >100° C, the coal would be assigned a low self-heating potential.

Correlation coefficients were also calculated for the undried samples using the same variables as for the dried samples. For these undried samples, a size dependence was found when correlating the minimum SHT values with the various gases. In addition, the resultant models were not only functions of the respective amounts of O_2 adsorbed, but depended also on some of the other gases released by the coals over the 7 days. Accordingly, gas samples would be required at the end of the test, in addition to a total pressure drop measurement, to be a reliable predictor of the self-heating potential of a coal.

DISCUSSION

ADIABATIC OVEN STUDIES

The minimum SHT's of coal samples determined in the adiabatic oven have been used to rank the relative self-heating tendencies of coals (*4*). In general, the minimum SHT's of coals increase with increasing rank, which is related to the chemical composition of the coal. From the results in reference 4, a relative self-heating risk was assigned to coals based on the coal's minimum SHT.

Although sealed flask tests have been conducted for many years, no relative assignment of self-heating risk based on the results has been made. Because the sealed flask tests are relatively simple to run compared with the expensive and time-consuming adiabatic oven test, an attempt was made in this study to correlate the results from the sealed flask tests with the relative self-heating tendencies of coals as determined in the adiabatic oven. If a correlation existed between the sealed flask results and the adiabatic oven results, a field-usable sealed flask apparatus could be designed.

The six coals chosen for study were selected to cover the range of self-heating tendencies from high to low, as determined in the adiabatic oven. The coals were selected from the set of coals evaluated in reference 4. The results differed slightly from those found in that study, but were still in the range of tendencies desired. The largest difference was for the Mary Lee coal, which had a minimum SHT of 135° C in reference 4, compared with a minimum SHT of 105° C in this study, but still within the range of low self-heating tendency. This difference in these two experimental minimum SHT values is attributed to the variation of coal composition within the seam, which can be seen in comparing the coal analyses of the two samples. The Pocahontas 3 sample also had a minimum SHT of 105° C, compared with 110° and 115° C in the previous study (*4*). The F and No. 80 coals had minimum SHT's of 35° C, within 10° C of the results from the previous study, and the No. 6 coal had a minimum SHT of 65° C in this study, compared with 70° C in the previous study. These three coals had a high self-heating potential based on the adiabatic oven tests. Finally, the Pittsburgh coal had a minimum SHT of 85° C, compared with 90° C previously (*4*) and thus a medium spontaneous combustion potential.

SEALED FLASK STUDIES

Effect of Particle Size on Oxygen Adsorption

The literature on the amount and rate of O_2 adsorption as a function of particle size contains conflicting results. Evidently, the type of coal used and its method of preparation can influence the results to a large extent. Conflicting results are likewise seen in this study for the undried and dried Pittsburgh, Pocahontas 3, and Mary Lee coals.

Undried Samples

A particle size effect could not be discerned for No. 80, F, and No. 6 coals. More O_2 was needed to ascertain the presence or absence of a particle size effect. To identify such an effect, tests should be conducted with smaller samples or with larger flasks. The sample size of 50 g was chosen to give a representative sample of the coal in each test. The flask size was double the size used in earlier Bureau tests (*3*), and gas samples were not taken during the tests to minimize O_2 depletion.

The only coal that showed a clear effect of size on O_2 adsorption was Mary Lee, although the effect observed, whereby the finer particles adsorbed the least, was the reverse of the one expected. The same trend was seen for Pocahontas 3 coal, but to a much smaller extent. The one coal that showed the expected trend, however small, was Pittsburgh coal. The flasks were stationary and were not shaken during the tests, so perhaps only the exposed, upper surfaces of the coal samples adsorbed O_2, while diffusion into the sample layer was slow. Yet, the first two size fractions (1,200 by 600 μm and 600 by 300 μm) were relatively coarse and air should have diffused easily through them. On the other hand, it is more probable that the outer surfaces of the coal particles are not the major adsorbing surfaces; rather, the inner surfaces of the micropores, which are probably the same for all the size fractions tested, are the adsorbing surfaces. When these micropores are filled or covered with an adsorbed monolayer or layers of water, the active sites are not available to react with O_2. One other factor that may contribute to such results is the adherence of fine particles to the coarse particles, thereby increasing their total surface area.

Dried Samples

As with the undried samples, smaller samples of the dried No. 80 coal, or larger volumes of air, would have helped to clarify the presence or absence of a size effect on O_2 adsorption. F coal appeared to have had enough O_2, but might also have adsorbed more if available. With regard to the other four coals, only No. 6 showed the expected results, an inverse relationship between particle size and amount of O_2 adsorbed. The reverse trend was found for the Pocahontas 3, Mary Lee, and Pittsburgh coals. The same explanations given with respect to the

results for the undried coals could be used for the results for the dried coals. Removal of moisture by drying should have emptied the micropores and uncovered the reactive sites. Apparently, the temperature of 67° C used in the drying step, together with flushing with N_2, is not sufficient for the removal of the final amounts of surface water adsorbed on the walls of the finer capillaries. Hippo (*33*) has shown that coals dried by conventional techniques retain tightly bound water and that the low rank coals retain more water than the higher ranked coals. Katz (*34*) reviewed results of some researchers regarding the effect of moisture on the amount of O_2 adsorbed and indicated that the various conclusions were inconsistent and were influenced by the mode of drying.

Unquestionably, the grinding and drying procedures used to prepare the coals can have a major influence on the adsorption and release of the various gases. Drying in vacuum is known to cause collapse of the micropores. Polat (*35*) measured the adsorption of O_2 by coal using a microbalance. He utilized four fractions (minus 100- plus 150-mesh, minus 200- plus 250-mesh, minus 300- plus 350-mesh, and minus 100- plus 350-mesh), and a regression analysis of his results showed no particle size dependence. Polat stored and ground the coal in water and dried it in vacuum, which may have contributed to the collapse of the micropores.

The effects of grinding on the results are also important. Coals typically contain various microlithotypes (vitrinite, inertinite, etc.), shaley material, and minerals. Each constituent has its own hardness and, as a result, its own characteristic grindability. In many cases the fines contain less ash than the coarse fractions (*36*), although the opposite has also been reported. If some of the minerals act as oxidation catalysts, their presence in greater abundance in the coarse fractions could explain some of the particle size effects on O_2 adsorption. Also, coal has a low compressive strength and possesses some degree of viscoelasticity. These characteristics can cause agglomeration and pelleting during extensive grinding, which minimizes O_2 adsorption by fine particles (*37*). The presence of different gases such as CO_2, CH_4, and H_2 (hydrogen) in the coal affects its hardness to different degrees and, as a result, its grindability (*38*). And lastly, in tests in which heat of wetting and vapor adsorption on coal powders were measured, it was found that the usual methods of grinding did not produce an appreciable extent of new surfaces, while prolonged grinding in a ball mill created fresh internal and external surfaces and increased the adsorption abilities of the coal powders (*39*).

These results suggest that in a sealed flask test the coarse size fraction will do well and may actually be more representative of the coal.

Comparison With Results in Literature

Coal preparation procedures, including grinding and drying methods, affect the O_2 adsorption of coal. Test conditions also influence the amount of O_2 adsorbed to a large extent. In dynamic test procedures in which a fresh flow of air continuously passes through the coalbed, the oxidation products (CO, CO_2, and H_2O) are flushed out. These products, singly or in combination, have been cited as capable of inhibiting the oxidation reaction. Thus, in a static test in which these products accumulate inside the flask, a quasi-equilibrium is attained in a much shorter time. In a few tests in this study and in additional tests with other coals, in which the atmosphere inside the flask was exchanged with fresh air at the end of the test, the adsorption of O_2 was resumed, though at a lower rate, in agreement with results of other researchers. For this reason, the relative sizes of the reaction vessel and the sample also affect the amount of O_2 adsorbed.

Because all these parameters, as well as others such as the test temperature, O_2 partial pressure, relative humidity of the test atmosphere, and the time at which samples are taken vary, it is difficult to compare the present results with those of others. According to results quoted by Winmill (*11*), the rate of O_2 adsorption decreases more rapidly for fine coal particles, so that after a sufficient time has elapsed, both fine and coarse coal samples will have consumed the same amount of O_2 (in weight percent) in a dynamic test setup. A characteristic rate of O_2 adsorption in air at ambient temperature, at a time when each sample has consumed 1 pct of its weight of O_2, was proportional to the cube root of the specific surface area of the sample. This time is different for the different size fractions, and thus continuous and long-time monitoring is needed to obtain these data. In this study, gas samples were taken only once and at the same time for all the samples. To sum it all up, unless test conditions are very similar, only general comparisons can be made.

Gases Released in Sealed Flasks

There is much interest in the gases that are released by coals for the detection of incipient combustion, especially CO, CO_2, and hydrocarbons, which are related to the state of the coal and its temperature. Mine air is continuously monitored, and changes in concentrations of some of these gases are used to detect incipient heating and fires in mines (*40*).

Graham (*41*) was among the first to use ratios of gases adsorbed and released by coal for assessing and detecting the development of heatings in mines. He suggested the use of the following two ratios: (a) O_2 adsorbed-CO

produced and (b) CO_2 produced-CO produced, for identifying changes in the temperature of the coal. The Bureau used the CO index (CO produced-O_2 adsorbed, the reverse of the Graham ratio) values to rank coals as to their relative propensities to self-heat. Dried coals with CO index values >180 were suggested as having high self-heating potentials (*3*).

In this study, the large quantities of CO_2 and CH_4 released by the undried samples stand out as compared with the respective amounts given off by the dried samples. It would appear that CO_2 is combined with the water in the coal in some way, and when water is removed, the CO_2 is removed with it. The solubility of CO_2 in water is much higher than the solubilities of the other gases found in the sealed flasks. For comparison, volumes of gas soluble in one volume of water, at 1 atm partial pressure and 20° C, are as follows (*42*):

Gas	*Solubility*
CO_2	0.872
CO	.023
O_2	.031
N_2	.016
CH_4	.033

Schafer (*43*) has shown that at least for low rank coals, the moisture content of the coal is directly related to its carboxyl content, and these oxygen-containing groups exert a controlling influence on the adsorbed water. When water is removed from the coal, the broken hydrogen bonds that held the water may contribute to the release of CO_2 from the -COOH groups (*43*). This indicates that a portion of the CO_2 gases released by the undried coal is not due to the formation of CO_2 by reaction of the O_2 adsorbed with the coal, but rather due to exchange and diffusion phenomena. These gases must have been present on the coal prior to the tests in the flasks. In adsorption tests with $^{18}O_2$-Ar atmospheres at ambient temperature, the amounts of $C^{18}O$ and $C^{18}O^{18}O$ released by Pittsburgh and Somerset (bituminous, Colorado) coals were minimal as compared with the amount of $C^{16}O^{16}O$ evolved ($C^{16}O$ was not determined) (*3*). These results imply, as mentioned above, that the gases desorbed by the coals have already been present on the coal before exposure of the samples to the test atmospheres. In addition to dissolution in water and the formation of carbonic acid (H_2CO_3), it is generally agreed that CO_2 also dissolves in coal itself (*44*). Measured surface areas of coals are much higher when CO_2 at 25° C is used as a probe than those found with N_2 at low temperature, or with various solvents at ambient temperatures (*45*).

During the coalification stages from cellulose and lignin to the various ranks of coal, CO_2, CH_4, and H_2O are formed. Some portions of these gases are retained in the coal and released when the virgin coal is broken. It is therefore not surprising to find the various coals releasing all kinds of gases, including CO_2, CH_4, CO, and H_2O. For the coals that contained CH_4, the amounts of CH_4 desorbed by them were much higher than the combined amounts of all the other gases. As to the effect of moisture in coal on CH_4 content, it is found that the capacity of coal to sorb and hold CH_4 is reduced by the presence of moisture (*46*). There is, though, a critical moisture content, characteristic of a coal, such that moisture in excess of this value has no further effect on CH_4 adsorption (*47*).

CO index values calculated for all the test samples show the following general trends: Values for dried coals are higher than for undried samples, and values for the fine size fractions are higher than for the coarse ones. Also, the two coals that adsorbed the largest amounts of O_2 and released the largest amounts of CO had the highest CO indices. However, if the results from the tests with isotopic O_2 are to be considered, then the amounts of CO released are not directly related to the amounts of O_2 adsorbed, and hence are not an indication of a current coal oxidation and the resultant, associated self-heating. Instead, CO indices signal previous oxidations and/or an increase in coal temperature, not specifically due to oxidation.

CORRELATION OF MINIMUM SELF-HEATING TEMPERATURE WITH OXYGEN ADSORBED AND PRESSURE DROP

A good correlation was found between the minimum SHT values and the amounts of O_2 adsorbed in the sealed flask tests, which was independent of particle size, for the dried samples as seen in equation 1. Thus, a sample of coal, crushed to <1,200 μm, and dried in an N_2 atmosphere, can be tested in a sealed flask, and the amount of O_2 adsorbed in 7 days can be used to determine the minimum SHT value for the coal. Sampling of the atmosphere is not necessary; the change in pressure, read in millivolts by the miniature pressure transducer (and calculated to an equivalent value in millimeters of mercury), can be used to calculate the minimum SHT using equation 2.

The results of correlations of minimum SHT and gaseous atmospheres in the flasks for the undried coals were not as successful, in that a simple correlation between the

minimum SHT and amounts of O_2 adsorbed was not found. Instead, a separate correlation was obtained for each fraction, and the minimum SHT was found to be dependent on other gases, such as CO, CH_4, CO_2, or combinations of these, in addition to O_2.

One major reason for these results for the undried samples was the large amount of CH_4 released in the flasks by four of the six coals tested. However, when the coals were ground to finer sizes, especially to the finest fraction, most of the CH_4 was released during the grinding and preparation, and smaller amounts were found in the flasks. A second reason for the lack of correlation between the minimum SHT's and the sealed flask test results for the undried samples was that the No. 80, F, and No. 6 coals adsorbed all the available O_2, and may have adsorbed more, before reaching an equilibrium state. Had more O_2 been available, the difference in reactivity between the No. 80 and F coals compared with the No. 6 coal may have been discerned and a better correlation may have resulted.

The good agreement between the minimum SHT values and results found for the dried samples is understandable. The coal samples for both tests were prepared in the same manner; they were ground, sieved, and then dried at 67° C, in an N_2 atmosphere for equal amounts of time. Accordingly, the coals underwent similar changes during the preparation phases. However, some unexpected results were observed for No. 6 and the coarse fractions of Mary Lee. These samples adsorbed less O_2 than the undried samples. Either these samples shrank during the drying phase and the pores collapsed, thus excluding O_2 from the micropore structure, or the presence of water was more crucial for these two coals. These two coals contained the largest amounts of ash, 21.4 and 12.0 pct, respectively, of the six coals. Water and/or the inorganic compounds may act as catalysts for the coal oxidation and in the absence of either one or both, the oxidation rate is reduced.

Another factor that contributed to the better correlation for the dried samples was the availability of a sufficient amount of O_2 for adsorption by the coals. All the coals, with the exception of No. 80, attained equilibrium in the 7 days. In the case of the undried samples, three coals—No. 80, F, and No. 6—probably would have adsorbed more O_2 were it available. Lastly, another contributing parameter was the size of the sample. In the dried samples, 50 g of coal was present in each test. In the undried samples, the amounts of the coal substance itself varied, depending on the amount of moisture in each coal.

To improve correlations for the undried samples, smaller samples of coal (e.g., 30 or 40 g) and/or larger flasks containing more O_2 than these coals could adsorb are needed.

Oxygen adsorption tests under similar static isothermal conditions were conducted by Chakravorty (*48*), with the goal of developing a simple test for classifying the liability of different coals to spontaneous combustion. For these tests, 50-g samples were placed in containers of about 2 L in volume. To eliminate the effect of CH_4, another 50-g sample was placed in an equivalent container in an inert atmosphere. The differential pressure drop between the two containers was recorded, and head gas was analyzed after 96 h. The same coals were also tested in an apparatus to determine their CPT's. Because of some anomalous CPT results for the high moisture coal samples, a correlation between pressure drop and CPT was not attempted. It is also not clear if the atmosphere in the container with the inert gas was tested, as well, to see if CH_4 was not released from the coal. In general, pressure drop values were deemed a good indicator of coal liability to spontaneous combustion. Chandra (*25*) reached the same conclusions regarding CPT, namely that it could not be used reliably to classify coals as to their proneness to spontaneous combustion.

CONCLUSIONS

Tests were conducted in the adiabatic oven and in sealed flasks with a suite of six bituminous coals, which ranged from a low to a high self-heating potential. Both undried and dried samples of four particle size ranges were tested in the sealed flasks.

An excellent correlation was found between the minimum SHT values, determined in the adiabatic oven, and the respective amounts of O_2 adsorbed by the dried coals after 7 days of exposure, as shown in equation 1. This correlation was independent of particle size. Likewise, a good correlation was found between the minimum SHT values and the pressure changes in the flasks after 7 days, ΔP_7, using miniature pressure transducers, as expressed in equation 2.

Correlations were not found for the undried samples. The large amount of CH_4 released by four of the coals was partly responsible. A second factor was the lack of sufficient O_2 required by the lower ranked coals to attain equilibrium in the flasks.

Based on the results obtained in this study, a prototype sealed flask apparatus can be developed that can be used to predict the self-heating potential of a bituminous coal.

REFERENCES

1. Nandy, D. K., D. D. Banerjee, and R. N. Chakravorty. Application of Crossing Point Temperature for Determining the Spontaneous Heating Characteristics of Coal. J. Mines, Met. and Fuels, v. 20, Feb. 1972, pp. 41-48.

2. Banerjee, S. C., and R. N. Chakravorty. Use of DTA in the Study of Spontaneous Combustion of Coal. J. Mines, Met. and Fuels, v. 15, Jan. 1967, pp. 1-19.

3. Kuchta, J. M., V. R. Rowe, and D. S. Burgess. Spontaneous Combustion Susceptibility of U.S. Coals. BuMines RI 8474, 1980, 37 pp.

4. Smith, A. C., and C. P. Lazzara. Spontaneous Combustion Studies of U.S. Coals. BuMines RI 9079, 1987, 28 pp.

5. Davis, J. D., and J. F. Byrne. An Adiabatic Method for Studying Spontaneous Heating of Coal. J. Am. Ceram. Soc., v. 7, No. 11, 1924, pp. 809-816.

6. Elder, J. L., W. A. Schmidt, S. A. Steiner, and J. D. Davis. Relative Spontaneous Heating Tendencies of Coals. BuMines TP 681, 1945, 24 pp.

7. Cudmore, J. F. Determination of Self-Heating Rates of Coal. Chem. & Ind. (London), Oct. 10, 1964, pp. 1720-1721.

8. Moxon, N. T., and S. B. Richardson. Development of a Calorimeter To Measure the Self-Heating Characteristics of Coal. Coal Prep., v. 2, No. 2, 1985, pp. 79-90.

9. Stonhardt, J. A. Calorimeter Design and the Assessment of Self-Heating in Coal. The Coal J., Nov. 1984, pp. 79-85.

10. Guney, M., and D. J. Hodges. Adiabatic Studies of the Spontaneous Heating of Coal. Part 2. Colliery Guardian, v. 217, No. 3, 1969, pp. 173-177.

11. Winmill, T. F. The Adsorption of Oxygen by Coal—Part I. Trans. Inst. Min. Eng., v. 46, 1913, pp. 563-578.

12. Graham, J. I. The Normal Production of Carbon Monoxide in Coal Mines. Trans. Inst. Min. Eng., v. 60, 1920-21, pp. 222-231.

13. Carpenter, D. L., and D. G. Giddings. The Initial Stages of the Oxidation of Coal With Molecular Oxygen I—Effect of Time, Temperature and Coal Rank on Rate of Oxygen Consumption. Fuel, v. 43, 1964, pp. 247-266.

14. Carpenter, D. L., and G. D. Sergeant. The Initial Stages of the Oxidation of Coal With Molecular Oxygen III—Effect of Particle Size on Rate of Oxygen Consumption. Fuel, v. 45, 1966, pp. 311-327.

15. Radspinner, J. A., and H. C. Howard. Determination of Surface Oxidation of Bituminous Coal. Ind. and Eng. Chem., Anal. Ed., v. 15, No. 9, 1943, pp. 566-570.

16. Banerjee, S. C., B. D. Banerjee, and R. N. Chakravorty. Rate Studies of Aerial Oxidation of Coal at Low Temperatures (30° - 170° C). Fuel, v. 49, No. 3, 1970, pp. 324-331.

17. Calahorro, C. V., A. B. Garcia, M. M. Gallego, and M. C. F. Gonzalez. Oxygen Chemisorption by an Anthracite From Penarroya (Spain). A Comparative Study Using Dynamic and Isothermal Gravimetric Methods. Thermochim. Acta, v. 96, 1985, pp. 69-79.

18. Münzner, H., and W. Peters. Zur Kinetik der Kohleoxydation im Temperaturbereich 30° C - 100° C (The Kinetics of Coal Oxidation in the Temperature Range 30° C - 100° C). Brennst. Chem., v. 46, 1965, pp. 399-407.

19. Howard, H. C. Low Temperature Reactions of Oxygen on Bituminous Coal. Trans. Am. Inst. Min. and Metall. Eng., Coal Div., v. 177, 1948, pp. 523-534.

20. Young, B. C., and P. Nordon. Method for Determining the Rate of Oxygen Sorption by Coals and Chars at Low Temperatures. Fuel, v. 57, No. 9, 1978, pp. 574-575.

21. Wade, L., M. J. Gouws, and H. R. Phillips. An Apparatus To Establish the Spontaneous Combustion Propensity of Coal. Paper 7.1 in Proceedings of Symposium on Safety in Coal Mining. Counc. Sci. and Ind. Res., 1987, 16 pp.

22. Guney, M., and D. J. Hodges. Adiabatic Studies of the Spontaneous Heating of Coal. Part 1. Colliery Guardian, v. 217, No. 2, 1969, pp. 105-109.

23. Humphreys, D., D. Rowlands, and J. F. Cudmore. Spontaneous Combustion of Some Queensland Coals. Paper in Proceedings of Symposium on Ignitions, Explosion and Fires in Coal Mines. Australas. Inst. Min. and Metall., Parkville, Victoria, 1981, 19 pp.

24. Bagchi, S. An Investigation on Some of the Factors Affecting the Determination of Crossing Point of Coals. J. Mines, Met. and Fuels, v. 13, Aug. 1965, pp. 243-260.

25. Chandra, D., S. K. Bhattacharya, R. Ghosh, and N. Dasgupta. On Evaluation and Classification of Coal With Respect to Proneness to Spontaneous Combustion. Q. J. Geol., Min. and Metall. Soc. India, v. 55, No. 3, 1983, pp. 130-136.

26. Kim, A. G. Laboratory Studies on Spontaneous Heating of Coal. A Summary of Information in the Literature. BuMines IC 8756, 1977, 13 pp.

27. Chamberlain, E. A. C., and D. A. Hall. The Liability of Coals to Spontaneous Combustion. Colliery Guardian, v. 221, Feb. 1973, pp. 65-72.

28. Van Doornum, G. A. W. The Spontaneous Heating of Coal. J. Inst. Fuel, v. 27, Oct. 1954, pp. 482-495.

29. Lowry, H. H. (ed.). Chemistry of Coal Utilization. Wiley, Suppl. V. 1963, pp. 272-276.

30. American Society for Testing and Materials. Standard Classification of Coals by Rank. D388-82 in 1983 Annual Book of ASTM Standards: Section 5, Petroleum Products, Lubricants, and Fossil Fuels: Volume 05.05, Gaseous Fuels; Coal and Coke. Philadelphia, PA, 1983, pp. 240-244.

31. Draper, N. R., and H. Smith. Applied Regression Analysis. Wiley, 1966, 178 pp.

32. BBN Research Systems. RS/1 User's Guide Book 2. Graphics and Statistics. Bolt Beranek and Newman Inc., Cambridge, MA, 1983, pp. 187-194.

33. Hippo, E. J., R. C. Neavel, S. E. Smith, R. J. Lang, and R. N. Miller. The Measurement of Water Tightly Bound by Low Rank Coals. Prep. Pap.—Am. Chem. Soc., Div. Fuel Chem., v. 32, No. 1, 1987, pp. 179-184.

34. Katz, S. H., and H. C. Porter. Effects of Moisture on the Spontaneous Heating of Stored Coal. BuMines TP 172, 1917, 25 pp.

35. Polat, S., and I. J. Harris. Low-Temperature Oxidation of Victorian Brown Coal. Fuel, v. 63, No. 5, 1984, pp. 669-672.

36. Agus, F., and P. L. Waters. Predicting the Grindability of Coal/Shale Mixtures. Fuel, v. 51, No. 1, 1972, pp. 38-43.

37. Celik, M. S. A Comparison of Dry and Wet Fine Grinding of Coals in a Ball Mill. Powder Technol., v. 55, No. 1, 1988, pp. 1-9.

38. Ettinger, I. L., and E. G. Lamba. Gas Medium in Coal-Breaking Processes. Fuel, v. 36, 1957, pp. 298-306.

39. Dresel, E. M., and M. Griffith. The Significance of the Heats of Wetting of Coal Powders Ground to Various Degrees of Fineness. Fuel, v. 28, No. 9, 1949, pp. 193-199.

40. Burgess, D., and H. H. Hayden. Carbon Monoxide Index Monitoring System in an Underground Coal Mine. Trans. Soc. Min. Eng. AIME, v. 260, 1976, pp. 312-317.

41. Graham, J. I. The Absorption of Oxygen by Coal. Part V—The Influence of Temperature on the Rates of Absorption by Different Parts of the Barnsley Bed. Trans. Inst. Min. Eng., v. 48, 1914-15, pp. 521-534.

42. Atack, F. W., and D. R. Atack (eds.). Handbook of Chemical Data. Reinhold, 1957, pp. 143-146.

43. Schafer, H. N. S. Factors Affecting the Equilibrium Moisture Contents of Low-Rank Coals. Fuel, v. 51, No. 1, 1972, pp. 4-9.

44. Reucroft, P. J., and A. R. Sethuraman. Effect of Pressure on Carbon Dioxide Induced Coal Swelling. Energy & Fuels, v. 1, No. 1, 1987, pp. 72-75.

45. Fowkes, F. M., K. L. Jones, G. Li, and T. B. Lloyd. Surface Chemistry of Coal by Flow Microcalorimetry. Energy & Fuels, v. 3, No. 1, 1989, pp. 97-105.

46. Graham, J. I. The Adsorption or Solution of Methane and Other Gases in Coal, Charcoal, and Other Materials. Trans. Inst. Min. Eng., v. 62, 1922, pp. 298-325.

47. Joubert, J. I., C. T. Grein, and D. Bienstock. Sorption of Methane in Moist Coal. Fuel, v. 52, No. 7, 1973, pp. 181-185.

48. Chakravorty, R. N., K. Kar, and N. Mansour. Categorization of Western Canadian Coals With Respect to Their Susceptibility to Spontaneous Combustion. Can. Cent. Miner. and Energy Technol. CANMET Rep. CRL 88-65(OP), 1988, 25 pp.

*U.S. Government Printing Office: 1990 — 511-010/40008